Thermodynamic Parameters for Ionisation and Dissociation of Alkyl Halides in Water and Nonaqueous Solvents. Comments on the Ion-pair Mechanism of Nucleophilic Substitution[1]

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Values of ΔG^0, ΔH^0, and ΔS^0 have been calculated by the appropriate thermodynamic cycle for the ionisation of alkyl halides to the ion-pair R^+X^- and for the dissociation of alkyl halides to the pair of ions $R^+ + X^-$, in water and in nonaqueous solvents. It is shown that values of ΔG^0 and ΔH^0 for ionisation of methyl and ethyl halides are so much higher than the observed values of $\Delta G^\ddagger$ and $\Delta H^\ddagger$ for solvolysis that it is energetically quite improbable that these halides undergo solvolysis or other nucleophilic substitutions by an ion-pair mechanism. For the isopropyl halides, ΔG^0 and ΔH^0 for ionisation are only slightly higher (by 1—5 kcal mol^{-1}) than $\Delta G^\ddagger$ and $\Delta H^\ddagger$ for solvolysis, so in view of the experimental error in the calculated values it is just possible that simple secondary halides might undergo solvolysis by an ion-pair mechanism. Values of ΔG^0 and ΔH^0 for ionisation of t-butyl halides are less than $\Delta G^\ddagger$ and $\Delta H^\ddagger$ for solvolysis, thus indicating an S_N1 or ion-pair-like transition state. This is confirmed by the marked correlation between the ionisation and activation parameters (G, H, and S) for reaction in six polar solvents.

Sneen and Larsen's[2] unified ion-pair mechanism of nucleophilic substitution has aroused widespread comment. Criticisms[3,4] of Sneen's original treatment have been answered by Sneen and Robbins;[5] it now appears that it is difficult (if not impossible) to distinguish between the ion-pair mechanism and the classical S_N1–S_N2 scheme by kinetic methods.[3-5] Results on the solvolysis of 1-methylheptyl methanesulphonate in aqueous dioxan can only be accommodated into the classical scheme, however, by the assumption of unusual negative normal salt-effects of added azide ion,[5] and for solvolysis of a number of s-alkyl substrates the ion-pair mechanism seems to be a reasonable alternative to the S_N1–S_N2 scheme.[5,6]

The possibility that even primary and methyl substrates might undergo nucleophilic substitution by the ion-pair mechanism was put forward by Sneen and Larsen,[2] but other workers have insisted that the solvolysis of *p*-nitrobenzyl chloride in aqueous acetone,[7] the substitution of *p*-nitrobenzyl chloride by trimethylamine in a variety of solvents,[8] and nucleophilic substitutions of bromoacetic acid in water,[9] proceed by S_N2 reactions and not by ion-pair mechanisms. However, Scott[10] has suggested that methyl halides in aqueous solution react by the ion-pair mechanism, and Scott and Robertson[11] later used this mechanism in the interpretation of nucleophilic substitutions of the methyl halides. Koskikallio[12] has also postulated an ion-pair mechanism for nucleophilic substitutions of methyl nitrate, perchlorate, and benzenesulphonate in water. For the aqueous hydrolysis of the methyl halides there is now the remarkable situation that charge separation, z, in the transition state is claimed (i) to be[13] close to zero, $z \simeq 0$, (ii) to be[14] quite small, $z = 0{\cdot}3$, and (iii) to be[10] very large, $z = 0{\cdot}76$—$0{\cdot}87$.

In its simplest form, the ion-pair mechanism reduces

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[1] Preliminary communication, M. H. Abraham, *Chem. Comm.*, 1973, 51.

[2] R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, 1969, **91**, 362, 6031.

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[9] J. L. Kurz and J. C. Harris, *J. Amer. Chem. Soc.*, 1970, **92**, 4117.

[10] J. M. W. Scott, *Canad. J. Chem.*, 1970, **48**, 3807.

[11] J. M. W. Scott and R. E. Robertson, *Canad. J. Chem.*, 1972, **50**, 167.

[12] J. Koskikallio, *Acta Chem. Scand.*, 1972, **26**, 1201.

[13] J. L. Kurz, *Accounts Chem. Res.*, 1972, **5**, 1.

[14] M. H. Abraham and G. F. Johnston, *J. Chem. Soc.* (*A*), 1971, 610.

to equations (1) and (2), where R^+X^- is an ion-pair that is attacked by the nucleophile N; the latter may be a

$$RX \rightleftharpoons R^+X^- \qquad (1)$$

$$R^+X^- + N \longrightarrow \text{Products} \qquad (2)$$

solvent molecule. Scott[10] suggested that for substitutions of the methyl halides in water, $k_{obs} = K_1 \cdot k_2$ so that $\Delta G^{\ddagger}_{obs} = \Delta G^0_1 + \Delta G^{\ddagger}_2$, where ΔG^0_1 is the standard free energy change for reaction (1) and $\Delta G^{\ddagger}_2$ is the free energy of activation for reaction (2). It therefore follows that $\Delta G^{\ddagger}_{obs} > \Delta G^0_1$ and Scott[10] deduced values of ΔG^0_1 that were indeed much lower than the observed free energies of activation for nucleophilic substitutions. Although more complicated than equations (1) and (2), Koskikallio's[12] proposed ion-pair mechanism still requires the above inequality. If the ion-pair mechanism did apply to S_N reactions of the methyl halides (the least likely substrates to react *via* ion-pairs), the classical S_N1–S_N2 scheme could then be regarded as obsolete; clearly, other methods for the assessment of the feasibility of reaction (1) are required. In the present work, values of ΔG^0_1 have been calculated and compared with $\Delta G^{\ddagger}_{obs}$ for solvolysis. If the calculated value of ΔG^0_1 is greater than $\Delta G^{\ddagger}_{obs}$ then it is evident that the ion-pair cannot lie on the reaction path from substrate to solvolysis product. The same reasoning applies to other nucleophilic reactions as well as to solvolyses.

Theory of the Method.—Equations (3)—(9) when summed give the ionisation reaction (1), and equations (3)—(8) give the dissociation reaction (10). The standard thermodynamic quantities for reactions (3)—(9) will thus yield corresponding values for both ionisation (1) and dissociation (10) of the substrate RX in solution. In the present work, standard states adopted will be 1 atm(g) and 1 mol l^{-1}(soln).

$$RX(\text{soln}) \longrightarrow RX(g) \qquad (3)$$

$$RX(g) \longrightarrow R\cdot(g) + X\cdot(g) \qquad (4)$$

$$R\cdot(g) \longrightarrow R^+(g) \qquad (5)$$

$$X\cdot(g) \longrightarrow X^-(g) \qquad (6)$$

$$R^+(g) \longrightarrow R^+(\text{soln}) \qquad (7)$$

$$X^-(g) \longrightarrow X^-(\text{soln}) \qquad (8)$$

$$R^+(\text{soln}) + X^-(\text{soln}) \longrightarrow R^+X^-(\text{soln}) \qquad (9)$$

$$RX(\text{soln}) \longrightarrow R^+(\text{soln}) + X^-(\text{soln}) \qquad (10)$$

This method has previously[15] been used to calculate values of ΔH^0_{10} in aqueous solution. An attempt was made by Franklin[16] to calculate ΔS^0_{10}, ΔH^0_{10}, and (hence) ΔG^0_{10}, but he used data that referred to the pure liquid solute in reaction (3), 80% aqueous methanol in reactions (7) and (8), and 80% aqueous ethanol in the solvolyses reactions to which his results were compared. No calculations of ΔG^0_1, ΔH^0_1, and ΔS^0_1 have hitherto been presented. Parameters for reactions (3)—(9) were obtained as follows.

Reaction (3). Values of ΔG^0_3, ΔH^0_3, and ΔS^0_3 are known[17] for the escape of methyl halides from water, and values of ΔG^0_3 for other alkyl halides can be deduced from their solubilities in water,[18] and their normal vapour pressures.[19] A value of ΔH^0_3 for t-butyl chloride from water can be obtained from the heat of solution of the liquid solute[20] (*ca.* +2 kcal mol^{-1}) * and its heat of vaporisation[22] (6·9 kcal mol^{-1}), whence $\Delta H^0_3 = +4{\cdot}9$ kcal mol^{-1}. Parameters for the escape of alkyl halides from a number of non-aqueous solvents are in Table 1.

TABLE 1

Thermodynamics of escape[a] of gaseous alkyl halides from some nonaqueous solvents at 298 K

Solute	Solvent	ΔG^0_3 [b]	ΔH^0_3 [c]	ΔS^0_3 [d]
MeI	Methanol	0·9 [e]	6·1 [f]	17·4
EtI	Methanol	1·7	6·9	17·4
Pr^iI	Methanol	1·9 [g]	7·4	18·5
Bu^tI	Methanol	2·0 [g]	7·8 [g]	19·5
Bu^tBr	Methanol	1·4	7·1	19·1
Bu^tCl	Methanol	1·1	6·6	18·4
Bu^tBr	Ethanol	1·5	7·1	18·7
Bu^tCl	Ethanol	1·1	6·6	18·4
Bu^tBr	Acetonitrile	1·7	6·6	16·4
Bu^tCl	Acetonitrile	1·3	6·2	16·4
Bu^tBr	Dimethylformamide	1·7	7·0	17·8
Bu^tCl	Dimethylformamide	1·3	6·4	17·1
Bu^tBr	Acetone	1·9	7·0	17·1
Bu^tCl	Acetone	1·6	6·5	16·4

[a] ΔG^0 and ΔH^0 in kcal mol^{-1}, ΔS^0 in cal K^{-1} mol^{-1}; standard states 1 atm. gas and 1 molar solution. [b] From data in ref. 30. [c] From calorimetrically determined heats of solution of liquid solutes, M. H. Abraham, unpublished observations, and calorimetrically determined heats of vaporisation from ref. 22. [d] From the ΔG^0_3 and ΔH^0_3 values. [e] R. Alexander, E. C. F. Ko, A. J. Parker, and T. J. Broxton, *J. Amer. Chem. Soc.*, 1968, **90**, 5049. [f] From the heat of solution of MeI(1), 0·49 kcal mol^{-1} (P. Haberfield, L. Clayman, and J. S. Cooper, *J Amer. Chem. Soc.*, 1969, **91**, 787), and the heat of vaporisation, 6·63 kcal mol^{-1}, from ref. 41. [g] Estimated values.

Reaction (4). ΔH^0_4 Values are available,[23] and ΔS^0_4 values may be calculated (Table 2); the corresponding ΔG^0_4 values are also in Table 2.

Reaction (5). ΔH^0_5 Values have been determined[24] and may be corrected by the entropy term $\Delta S^0_5 = -R \ln 2$ to give values of ΔG^0_5.

Reaction (6). McCoubray[25] has given ΔH^0_6 values which may again by corrected by the term $\Delta S^0_6 = -R \ln 2$ to give ΔG^0_6 values. Although McCoubray's

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* Arnett *et al.*[20] determined ΔH_s for $Bu^tCl(1)$ in various water–ethanol mixtures. Extrapolation to pure water is not easy and yields values from 1·5—2·5 kcal mol^{-1} (*cf.* the value of 3 kcal mol^{-1} used by Gold[21]).

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[18] N. C. Deno and H. E. Berkheimer, *J. Chem. Eng. Data*, 1960, **5**, 1.

[19] R. R. Dreisbach, 'Physical Properties of Chemical Compounds,' American Chemical Society, Washington, 1961.

[20] E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. McC. Duggleby, *J. Amer. Chem. Soc.*, 1965, **87**, 1541.

[21] V. Gold, *J.C.S. Faraday I*, 1972, 1611.

[22] I. Wadsö, *Acta Chem. Scand.*, 1968, **22**, 2438.

[23] J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465; S. W. Benson, *J. Chem. Educ.*, 1965, **42**, 502.

[24] F. P. Lossing and G. P. Semeluk, *Canad. J. Chem.*, 1970, **48**, 955.

[25] J. C. McCoubray, *Trans. Faraday Soc.*, 1955, **51**, 743.

electron affinities are not the most recent ones, they are consistent with the values used for $\Delta H^0{}_8$. Any amendment to the $\Delta H^0{}_6$ values will automatically be cancelled out in $\Delta H^0{}_8$.

Reactions (7) *and* (8). The data of Noyes [26] on the hydration of ions are used. Values for the hydration of carbonium ions were obtained from plots of hydration parameters against the cation molar volumes and are in Table 3. Since the cations used in such plots (Na^+, K^+, Rb^+, Cs^+, and Me_4N^+) are all closed-shell ions, the objection might be raised that such a procedure will not necessarily yield correct values for carbonium ions. There is evidence to show, however, that the obtained values of $\Delta P^0{}_7$ ($P = H$, G, and S) for carbonium ions are reasonable. (a) The value of $\Delta H^0{}_7$ for Me_3C^+ in water calculated by the present method ($-56{\cdot}5$ kcal mol^{-1}) compares well with that obtained by Gold [21] using an independent method (-59 kcal mol^{-1} on Noyes scale). (b) It is known that there is a close correspondence between solvent effects on the free energy of the t-butyl chloride transition state and of the ion-pair $Me_4N^+Cl^-$. Now since the transition state is close to the species $Me_3C^+Cl^-$ it follows that solvent effects on the free energy of $Me_3C^+Cl^-$ and of the closed-shell species $Me_4N^+Cl^-$ will also be similar. Since these solvent effects cover a wide range of solvents, it seems that solvation of $Me_3C^+Cl^-$ must be qualitatively and quantitatively similar to solvation of $Me_4N^+Cl^-$, so that the closed-shell cation Me_4N^+ is a reasonable model for the cation Me_3C^+ in terms of solvation behaviour. (c) In part (iii) of the Results and Discussion section, the present obtained values of $\Delta P^0{}_7$-(R^+) are combined with standard data to yield values of $\Delta P^0{}_f(R^+, aq)$. Such $\Delta P^0{}_f$ values can then be used to calculate ΔP^0 values for a number of processes involving carbonium ions in aqueous solution, and it is shown that the ΔP^0 values are in accord with available experimental data. Hence the original $\Delta P^0{}_7(R^+)$ values are again seen to be realistic values.

TABLE 2

Thermodynamic parameters [a] for the process $RX(g) \longrightarrow R{\cdot}(g) + X{\cdot}(g)$ at 298 K

RX	$\Delta G^0{}_4$ [b]	$\Delta H^0{}_4$ [c]	$\Delta S^0{}_4$ [d]
MeF	98·8	108·0	31·0
MeCl	74·6	83·5	29·9
MeBr	61·2	70·0	29·4
MeI	47·7	56·3	28·9
EtF	95·9	106·0	33·8
EtCl	71·7	81·5	32·8
EtBr	59·4	69·0	32·3
EtI	44·1	53·5	31·6
Pr^iF	94·4	105·0	35·7
Pr^iCl	70·7	81·0	34·4
Pr^iBr	57·9	68·0	33·9
Pr^iI	43·1	53·0	33·2
Bu^tF	91·1	102·0	36·6 [e,]
Bu^tCl	67·9	78·5	35·7 [e]
Bu^tBr	52·4	63·0	35·7 [e]
Bu^tI	39·2	49·5	34·6 [e]

[a] ΔG^0 and ΔH^0 in kcal mol^{-1}, ΔS^0 in cal K^{-1} mol^{-1}; standard state 1 atm. [b] From $\Delta H^0{}_4$ and $\Delta S^0{}_4$. [c] Ref. 23. [d] Calculated from data in refs. 40 and 41, and by J. H. Purnell and C. P. Quinn, *J. Chem. Soc.*, 1964, 4049. [e] Using an estimated value of $S^0 = 73{\cdot}2$ for the Bu^t radical. [f] With $S^0 = 74{\cdot}5$ for Bu^tF (G. Ya. Kabo and D. N. Andreevskii, *Zhur. fiz. Khim.*, 1971, 1021).

TABLE 3

Thermodynamic parameters [a] for the hydration of gaseous ions at 298 K

Ion	ΔG^0	ΔH^0	ΔS^0
F^-	−103·8 [b]	−114·0 [b]	−34·1
NO_3^-	−61·7 [c]	−68·0 [d]	−21 [c]
ClO_4^-	−44·6 [c]	−50 [c]	−19 [c]
H^+	−259·2	−267·9	−29·3
Me_4N^+	−44·1 [e]	−52·1 [e]	−26·7 [e]
Me^+	−73·0 [f]	−77·0 [f]	−13·4
$MeCH_2^+$	−60·0 [f]	−65·5 [f]	−18·4 [f]
Me_2CH^+	−54·0 [f]	−60·5 [f]	−21·8 [f]
Me_3C^+	−49·0 [f]	−56·5 [f]	−25·2 [f]

[a] ΔG^0 and ΔH^0 in kcal mol^{-1}, ΔS^0 in cal K^{-1} mol^{-1}; standard states 1 atm. gas and 1 molar solution. Data from ref. 26 except where indicated. [b] Ref. 25. [c] From G. A. Kreshkov, *Zhur. fiz. Khim.*, 1965, **39**, 823; *Teor i exp. Khim.*, 1965, **1**, 479. [d] From H. D. B. Jenkins and T. C. Waddington, *J. Inorg. Nuclear Chem.*, 1972, **34**, 2465. [e] From R. H. Boyd, *J. Chem. Phys.*, 1969, **51**, 1470. [f] Values estimated in this work.

For non-aqueous solvents, the hydration parameters of Noyes were combined with data [27] on the transfer of ions from water to the given solvents; values for carbonium ions were calculated as above.

In all the above calculations, cation molar volumes used were (ml mol^{-1}): Me^+ 15; $MeCH_2^+$ 31; Me_2CH^+ 47; Me_3C^+ 63. Since values of $\Delta P^0{}_7$ (M^+) do not vary very greatly with cation molar volume, use of slightly different molar volumes for R^+ would not lead to significantly different hydration parameters.

Reaction (9). Values of ion-pair association constants, K_A, are known for alkali halides,[28] and tetra-alkylammonium halides [29-34] in water and nonaqueous solvents.

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[32] C. de Visser and G. Somsen, *Rec. Trav. chim.*, 1972, **91**, 942.

[33] W. A. Adams and K. J. Laidler, *Canad. J. Chem.*, 1968, **46**, 1977, 2005.

[34] S. R. C. Hughes and D. H. Price, *J. Chem. Soc.* (*A*), 1968, 1464.

For each solvent, plots of K_A against the cation molar volume were constructed, treating the chlorides, bromides, iodides, nitrates, and perchlorates separately, and the required K_A (K_9) values estimated from the various plots. For salts of a given anion in a given solvent, values of K_A do not vary greatly with the cation molar volume. This procedure yields ΔG^0_9 values, but it is not so easy to obtain values for ΔS^0_9 and ΔH^0_9. For reaction (9; RX = Bu^{t}Cl and Bu^{t}Br), ΔS^0_9 was taken (in cal K^{-1} mol^{-1}) as 0 in water,[31] +9 in DMF,[32] and +14 in acetone,[33] and the corresponding ΔH^0_9 values derived from ΔS^0_9 and ΔG^0_9. Where values of ΔS^0_A (ΔS^0_9) are known, or can be calculated from literature data, for 1 : 1 electrolytes in polar or moderately polar solvents [31-34] it seems that approximately ΔS^0_A (cal K^{-1} mol^{-1}) = $4{\cdot}3\Delta G^0_A$ (kcal mol^{-1}); in this way values of ΔS^0_9 and hence of ΔH^0_9 were obtained from ΔG^0_9 values for all other cases. Where this procedure was used, ΔG^0_9 ranged from $+1{\cdot}5$ to $-2{\cdot}9$ kcal mol^{-1} and ΔS^0_9 from −6 to +12 cal K^{-1} mol^{-1} over the various solvents and solutes, so that the additional error in ΔS^0_9 introduced is probably not more than 2 or 3 units. Just as for reaction (7), data on closed-shell cations has been used, above. Where results can be checked against experimental data, as in the solvolyses of t-butyl halides, it seems again as though the method does yield realistic parameters for reaction (9).

TABLE 4

Calculation of thermodynamic parameters [a] for the ionisation and dissociation of alkyl halides, in water at 298 K

		MeF			MeCl			MeBr			MeI			Bu^{t}Cl		
	Process	ΔG^0	ΔH^0	ΔS^0	ΔG^0	ΔH^0	ΔS^0	ΔG^0	ΔH^0	ΔS^0	ΔG^0	ΔH^0	ΔS^0	ΔG^0	ΔH^0	ΔS^0
	(3)	−1·7	4·3	20·1	−1·3	5·6	23·2	−1·1	6·2	24·5	−1·0	6·2	24·1	−3·0 [b]	4·9	26·5
	(4)	98·8	108·0	31·0	74·6	83·5	29·9	61·2	70·0	29·4	47·7	56·3	28·9	67·9	78·5	35·7
	(5)	227·3	226·9	−1·4	227·3	226·9	−1·4	227·3	226·9	−1·4	227·3	226·9	−1·4	160·2	159·8	−1·4
	(6)	−81·8	−82·2	−1·4	−86·9	−87·3	−1·4	−81·6	−82·0	−1·4	−75·3	−75·7	−1·4	−86·9	−87·3	−1·4
	(7)	−73·0	−77·0	−13·4	−73·0	−77·0	−13·4	−73·0	−77·0	−13·4	−73·0	−77·0	−13·4	−49·0	−56·5	−25·2
	(8)	−103·8	−114·0	−34·1	−74·8	−80·9	−20·3	−67·9	−72·8	−16·3	−59·0	−62·4	−11·3	−74·8	−80·9	−20·3
Dissociation	(10)	65·8	66·0	0·8	65·9	70·8	16·6	64·9	71·3	21·4	66·7	74·3	25·5	14·4	18·5	13·9
	(9)	0·3	0·0	−1·0	0·7	−0·2	−3·0	1·3	−0·5	−6·0	1·5	−0·6	−7·0	0·1	0·1	0·0
Ionisation	(1)	66·1	66·0	−0·2	66·6	70·6	13·6	66·2	70·8	15·4	68·2	73·7	18·5	14·5	18·6	13·9

[a] ΔG^0 and ΔH^0 in kcal mol^{-1}, ΔS^0 in cal K^{-1} mol^{-1}; standard states 1 atm. gas and 1 molar solution. Data as given in the text, except where indicated. [b] From data in ref. 30.

TABLE 5

Comparison of thermodynamic parameters for dissociation (10) and ionisation (1) of alkyl halides with activation parameters for solvolysis, at 298 K [a]

RX	Solvent	ΔG^0_{10}	ΔH^0_{10}	ΔS^0_{10}	ΔG^0_1	ΔH^0_1	ΔS^0_1	$\Delta G^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
MeF	Water	66	66	1	66	66	0	30	27	−9
MeCl	Water	66	71	17	67	71	14	28	27	−4
MeBr	Water	65	71	21	66	71	15	26	25	−3
MeI	Water	67	74	25	68	74	19	27	27	1
EtF	Water	42			42					
EtCl	Water	42			43			27	26	−1
EtBr	Water	42			43			26	26	−2
EtI	Water	42			43			27	27	0
Pr^{i}F	Water	27			28					
Pr^{i}Cl	Water	28			28			27	26	−2
Pr^{i}Br	Water	27			28			25	26	3
Pr^{i}I	Water	28			28			25	27	7
Bu^{t}F	Water	14			14			26	24	−8
Bu^{t}Cl	Water	14	18	14	15	19	14	20	23	12
Bu^{t}Br	Water	11			11			18 [b]	22 [b]	15 [b]
Bu^{t}I	Water	14			14			17 [c]		
MeI	Methanol	73	70	−9	72	70	−5	29 [d]		
EtI	Methanol	49	47	−7	48	48	−1	29 [e]		
Pr^{i}I	Methanol	35	34	−4	33	34	3	28 [e]		
Bu^{t}I	Methanol	22	21	−2	20	22	6	23 [f]	22 [f]	−2 [f]
Bu^{t}Cl	Methanol	24	22	−8	23	22	−3	26 [b]	25 [b]	−3 [b]
Bu^{t}Br	Methanol	20	19	−4	19	19	2	24 [b]	24 [b]	0 [b]
Bu^{t}I	Methanol	22	21	−2	20	22	6	23 [f]	22 [f]	−2 [f]

[a] ΔG and ΔH in kcal mol^{-1}, ΔS in cal K^{-1} mol^{-1} rounded-off to the nearest whole number. Values for the activation parameters for hydrolysis in water from R. E. Robertson, R. L. Heppolette, and J. M. W. Scott, *Canad. J. Chem.*, 1959, **37**, 803, and R. L. Heppolette and R. E. Robertson, *Canad. J. Chem.*, 1966, **44**, 677. [b] From Table 8. [c] Footnote *h*, Table 8. [d] R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, 1968, **90**, 319. [e] Values estimated from $\Delta G^\ddagger$ in water with *m* as 0·3 (EtI) and 0·5 (Pr^{i}I). [f] Footnote *c*, Table 8.

RESULTS AND DISCUSSION

(i) *Reactions in Water and Methanol.*—A complete analysis in terms of *G*, *H*, and *S* may be carried out for reactions (1) and (10) with five alkyl halides in water (Table 4). Additional data are available for reactions in methanol, and in Table 5 are summarised the final results for calculation on reactions (1) and (10) in water and methanol. The absolute error in values of ΔG^0 and ΔH^0 for reactions (1) and (10) could be as much as 3 or 4 kcal mol^{-1}, and the absolute error in ΔS^0 as much as 5 cal K^{-1} mol^{-1}. However, the errors in relative values either for a given alkyl halide in different solvents or for different alkyl halides in the same solvent will be much less. Results (below) on reactions of Bu^tCl in different solvents suggest that relative errors in $\Delta G^0{}_1$ and $\Delta G^0{}_{10}$ could be as low as 0·3 kcal mol^{-1}.

Table 6

RX		MeF	MeCl	MeBr	MeI	EtCl	EtBr	EtI
$\Delta G^0{}_1$	(This work)	66	67	66	68	43	43	43
$\Delta G^0{}_1$	(Scott)	19	12	10	9			
$\Delta G^{\ddagger}{}_{obs}$	for hydrolysis	30	28	26	27	27	26	27

For primary alkyl halides the calculated values of $\Delta G^0{}_1$ and $\Delta H^0{}_1$ for the ionisation reaction (1) are far higher than the corresponding activation parameters for solvolysis and (for the methyl halides) far higher than Scott's[10] calculated $\Delta G^0{}_1$ values (kcal mol^{-1}) for ionisation in water (Table 6). With the $\Delta G^0{}_1$ values calculated in the present work, it follows that for primary alkyl halides $\Delta G^0{}_1 \gg \Delta G^{\ddagger}{}_{obs}$ and hence that the ion-pair cannot lie on the solvolysis reaction path. (The same conclusion is true also for other nucleophilic substitutions of the methyl and ethyl halides.) The differences $\Delta G^0{}_1 - \Delta G^{\ddagger}{}_{obs}$ are *ca.* 40 kcal mol^{-1} for the methyl halides and 15 kcal mol^{-1} for the ethyl halides in water, so that they are well outside the absolute error limits. It seems to be generally agreed, even by Sneen and Larsen,[2] that it is energetically not feasible for primary halides to dissociate into a pair of ions in common solvents (and the calculated values of $\Delta G^0{}_{10}$ and $\Delta H^0{}_{10}$ in Table 5 confirm this), so that of the set of reactions (3)—(9), only the association reaction (9) is left as a possible source of errors of the above magnitudes. Values of $\Delta G^0{}_9$ have been calculated from K_A values determined conductometrically. In such determinations both closed and solvent-separated ion-pairs will be counted together, whereas in his analysis Scott[10] specifically considered reaction to proceed *via* closed ion-pairs. However, since closed ion-pairs will constitute only some fraction of the total ion-pairs, values of K_A for association of a pair of ions to closed ion-pairs must be smaller than the observed K_A values and hence $\Delta G^0{}_9$ values for association to closed ion-pairs will be more positive than those used in the present calculations. Use of $\Delta G^0{}_9$ values for closed ion-pairs will therefore result in $\Delta G^0{}_1$ values more positive than those calculated here, and will accentuate the $\Delta G^0{}_1 - \Delta G^{\ddagger}{}_{obs}$ differences, observed for the methyl and ethyl halides. Sneen and Larsen[2] suggest that in some way ion-pairs derived from primary alkyl halides may be more stable than expected, but in order to reduce the $\Delta G^0{}_1$ value for, say, methyl iodide from 68 to 27 kcal mol^{-1} (the value of $\Delta G^{\ddagger}{}_{obs}$ for aqueous hydrolysis) the ion-pair association constant in reaction (9; RX = MeI) would need to be 10^{29} as compared with usual values for 1 : 1 electrolytes in water of less than unity! There seems no way in which the present calculations can be responsible for the observed discrepancy in the $\Delta G^0{}_1$ and $\Delta G^{\ddagger}{}_{obs}$ values for primary halides. Scott's values of $\Delta G^0{}_1$ differ from those calculated in the present work also by enormous margins (see above); his treatment involved the assumption that HO^- and H_2O react with cations Ar_3C^+ in water by simple unitary processes. However, Ritchie[35] has shown that the reaction of H_2O with Malachite Green is subject to general base catalysis and hence that attack of HO^- might be regarded as a HO^- catalysed attack of H_2O. If Scott's assumption is not valid, his calculated values of $\Delta G^0{}_1$ may thus not be at all correct.

Scott and Robertson[10,11] lay stress on the fact that Scott's calculated values of $\Delta G^0{}_1$ help to explain the peculiar sequence of hydrolysis rates in water, MeCl < MeBr > MeI. They claim that such a sequence in water is characteristic of a mechanism in which nucleophilic attack on an ion-pair is important (as, they suggest, for hydrolyses of MeX and Pr^iX), whereas the normal sequence in water, RCl < RBr < RI, is characteristic of a mechanism in which a closed ion-pair yields a solvent-separated ion-pair (as, they suggest, for hydrolyses of Bu^tX). However, Koskikallio[36] has observed the sequence RCl < RBr < RI for hydrolyses of the primary halides Bu^nX in water at 80, 60, 40, and on extrapolation at 25°. It would be a peculiar situation if halides Bu^nX and Bu^tX were held to hydrolyse by one type of mechanism and halides MeX and Pr^iX by another, so that doubt is cast on the use of the above reactivity sequences in water as a mechanistic criterion.

On the evidence of the present calculated values of $\Delta G^0{}_1$ and $\Delta H^0{}_1$, I conclude that methyl and ethyl halides do not undergo solvolyses or other nucleophilic substitutions by the ion-pair mechanism in solvents such as water, methanol, ethanol, dimethylformamide, acetonitrile, and acetone, and that charge separation in their solvolysis transition states must be very small (*cf.* refs. 13 and 14). Values of $\Delta G^0{}_1$ for the isopropyl halides are only slightly higher than values of $\Delta G^{\ddagger}{}_{obs}$ for solvolysis in water and methanol, and in view of the experimental error in $\Delta G^0{}_1$, it is just possible (though a little unlikely) that simple secondary alkyl halides undergo solvolysis by the ion-pair mechanism; for other secondary substrates the ion-pair mechanism could energetically be feasible. Calculated values of $\Delta G^0{}_1$ for the t-butyl halides are all less than the $\Delta G^{\ddagger}{}_{obs}$ values for corresponding solvolyses, so that an ion-pair mechanism can operate in these cases. For solvolyses of the t-butyl halides it has been shown[30] that the rate-determining step is reaction (1), so that $\Delta G^{\ddagger}{}_{obs} = \Delta G^{\ddagger}{}_1$. Since $\Delta G^{\ddagger}{}_1 > \Delta G^0{}_1$ it follows that $\Delta G^{\ddagger}{}_{obs} > \Delta G^0{}_1$, in agreement with the present calculations.

Approximate calculations on methyl, ethyl, and isopropyl nitrates show that values of $\Delta H^0{}_1$ for the nitrates

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[35] C. D. Ritchie, *J. Amer. Chem. Soc.*, 1972, **94**, 3275.

[36] J. Koskikallio, *Acta Chem. Scand.*, 1967, **21**, 397.

do not differ significantly from values for the corresponding halides, *e.g.* for reaction (1) in water ΔH^0_1 values (kcal mol^{-1}) are: MeI 74, EtI 50, Pr^iI 36; $MeNO_3$ 73, $EtNO_3$ 52, Pr^iNO_3 38. Thus neither methyl nitrate nor ethyl nitrate can hydrolyse in water by the ion-pair mechanism.

TABLE 7

Comparison of entropies (cal K^{-1} mol^{-1}) of activation for solvolyses in water and methanol with standard entropies (cal K^{-1} mol^{-1}) of ionisation of alkyl halides [reaction (1)] at 298 K

Solute	Solvent	$\Delta S^‡$	ΔS^0_1
Bu^tBr	Water	15 [a]	
Bu^tCl	Water	12 [a]	14 [a]
$MeClO_4$	Water	3 [b]	19 [c]
MeI	Water	1 [a]	
$MeNO_3$	Water	−3,[d] −1 [e]	
Bu^tBr	Methanol	0 [a]	2 [a]
Bu^tCl	Methanol	−3 [a]	−3 [a]
$MeClO_4$	Methanol	−20 [f]	−5 [c]
MeI	Methanol	−20 [g]	

[a] From Tables 5 and 8. [b] From $\Delta S^‡ = 5{\cdot}6$ at 12° (ref. 37) assuming $\Delta C^‡_p = -50$ cal K^{-1} mol^{-1}. [c] Approximate calculations suggest values for the perchlorate and nitrate will be close to those for the iodide. [d] From $\Delta S^‡ = -10{\cdot}8$ at 75° (S. Jokinen, E. Luukkonen, J. Ruostesuo, J. Virtanen, and J. Koskikallio, *Acta Chem. Scand.*, 1971, **25**, 3367), assuming $\Delta C_p^‡ = -50$ cal K^{-1} mol^{-1}. [e] From data by J. S. McKinley-McKee and E. A. Moelwyn-Hughes, *Trans. Faraday Soc.*, 1952, **48**, 247. [f] J. Koskikallio, *Suomen Kem.*, 1967, **40B**, 131. Note that the solvent contained *ca.* 4% cyclohexane. [g] At 75° from data by D. Cook, I. P. Evans, E. C. F. Ko, and A. J. Parker, *J. Chem. Soc.* (*B*), 1966, 404. The value at 25° will probably not differ by more than 1 or 2 units.

Calculated values of the entropy of ionisation, ΔS^0_1, are all large positive quantities for the alkyl halides (except the fluorides) in water, whereas in methanol values are much closer to zero. Koskikallio[37] at one time interpreted values of $\Delta S^‡_{obs}$ for the solvolysis of methyl perchlorate in water and methanol in terms of the classical S_N1–S_N2 scheme, reasoning that the positive value in water indicated the S_N1 mechanism and that the negative value of $\Delta S^‡_{obs}$ in methanol indicated the S_N2 mechanism. A comparison of $\Delta S^‡_{obs}$ values with calculated values of ΔS^0_1 is more instructive (see Table 7), and shows that although $\Delta S^‡_{obs}$ for solvolysis of methyl perchlorate in water is positive, it is still much more negative than the calculated value for ionisation. Of the listed substrates, only the t-butyl halides give rise to $\Delta S^‡_{obs}$ values that are close to the calculated values of ΔS^0_1, and I suggest that whereas the halides Bu^tX undergo solvolysis by an S_N1 or ion-pair mechanism, the substrates $MeClO_4$, $MeNO_3$, and MeI do so both in water and in methanol by a mechanism that is close to the S_N2 type of reaction.

TABLE 8

Comparison of thermodynamic parameters for dissociation (10) and ionisation (1) of t-butyl halides with activation parameters for solvolysis at 298 K [a]

RX	Solvent	ΔG^0_{10}	ΔH^0_{10}	ΔS^0_{10}	ΔG^0_1	ΔH^0_1	ΔS^0_1	$\Delta G^‡$	$\Delta H^‡$	$\Delta S^‡$
Bu^tCl	Water	14·4	18·5	14	14·5	18·6	14	19·5 [b]	23·1 [b]	12 [b]
Bu^tCl	Methanol	23·8	21·5	−8	22·6	21·8	−3	25·8 [c,d]	24·9 [c,d]	−3 [c,d]
Bu^tCl	Ethanol	26·6	21·2	−18	23·8	22·0	−6	27·1 [d]	26·1 [d]	−3 [d]
Bu^tCl	Acetonitrile	29·1	20·5	−29	26·8	21·2	−19	29·4 [e]	25·2 [f]	−14 [f]
Bu^tCl	Dimethylformamide	28·4	19·6	−29	26·1	20·2	−20	29·0 [g]	24·6 [g]	−15 [g]
Bu^tCl	Acetone	33·5	21·7	−40	29·6	22·0	−26	31·4 [e]		
Bu^tBr	Water	11·4			11·3			17·6 [h]	22·0 [h]	15 [h]
Bu^tBr	Methanol	20·2	19·0	−4	18·7	19·4	2	23·5 [c,i]	23·5 [c,i]	0 [c,i]
Bu^tBr	Ethanol	23·0	18·5	−15	20·1	19·3	−3	24·7 [i]	24·4 [i]	−1 [i]
Bu^tBr	Acetonitrile	23·3	15·5	−26	21·1	16·1	−17	25·4 [f]	22·5 [f]	−10 [f]
Bu^tBr	Dimethylformamide	22·7	14·0	−29	20·6	14·6	−20	25·1 [i]	21·9 [i]	−11 [i]
Bu^tBr	Acetone	26·9	15·9	−37	23·2	16·4	−23	27·2 [e]		

[a] ΔG and ΔH in kcal mol^{-1}, ΔS in cal K^{-1} mol^{-1}. [b] Footnote *a*, Table 5. [c] J. Biordi and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1962, 4291. [d] S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 5937. [e] Ref. 30. [f] Estimated values. [g] E. S. Rudakov and V. P. Tretyakov, *Reakts. spos. org. Soedinenii*, 1965, **2**, 142; S. D. Ross and M. M. Labes, *J. Amer. Chem. Soc.*, 1957, **79**, 4155. [h] E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1962, 4301. [i] P. O. I. Virtanen, *Suomen Kem.*, 1967, **40B**, 179.

(ii) *Solvolyses of the t-Butyl Halides.*—In Table 8 are the calculated parameters for reactions (1) and (10), and activation parameters for solvolyses, in six polar solvents. Parameters for the ionisation reaction (1), parallel strikingly the activation parameters. Plots of $\Delta G^‡_{obs}$ against ΔG^0_1 yield good straight lines of slopes 0·8 (Bu^tCl), and 0·8 (Bu^tBr), values close to those obtained[30] on plotting values of ΔG^0_t ($[Bu^tX]^‡$) values against of ΔG^0_t (Me_4NX), *viz.* 0·7 after correction for a small non-electrostatic effect.* There are also reasonable linear correlations between $\Delta S^‡_{obs}$ and ΔS^0_1, but the correlations between $\Delta H^‡_{obs}$ and ΔH^0_1 are not very good. This is partly because the variation in ΔH with solvent is less than that in ΔG and partly because $\Delta H^‡_{obs}$ is known much less accurately than is $\Delta G^‡_{obs}$. The present results, however, confirm that reaction (1) is a good model for the activation process, and that the transition states for solvolyses of the t-butyl halides lie between the halide and the ion-pair but very close to the ion-pair.

(iii) *Thermodynamics of Carbonium Ion Formation and Reactions.*—In the introduction, the use of data on closed-shell ions to deduce values of $\Delta P^0_7(R^+)$, where $P = H$, G, and S, was justified on a number of grounds, one of which was that the values of $\Delta P^0_7(R^+)$ so obtained led to realistic values for $\Delta P^0_f(R^+, aq)$. In

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* The values obtained in the present work should provide better estimates of charge separation in the transition state than those found[30] using the solutes $Me_4N^+X^-$ as comparative standards.

[37] J. Koskikallio, *Acta Chem. Scand.*, 1969, **23**, 1477.

TABLE 9

Thermodynamic parameters [a] for the formation of carbonium ions (g, 1 atm) at 298 K

	ΔG^0_f	ΔH^0_f	S^0	ΔH^0_f [b]	ΔH^0_f [c]
Me^+	262·0	261·0	45·0	261	
Et^+	226·3	219·5	57·8	219	(219)
Pr^{n+}	221·1	207·6	67·9	208	209
Pr^{i+}	205·5	191·5	66·2	192	190
Bu^{n+}		201·7		201	
Bu^{i+}		198·7		199	
Bu^{s+}		183·3		183	
Bu^{t+}	187·3	165·2	71·8	167	163

[a] ΔG^0_f and ΔH^0_f in kcal mol^{-1}, S^0 in cal K^{-1} mol^{-1}; this work except where indicated. [b] Ref. 24. [c] Theoretically calculated values (ref. 39).

TABLE 10

Thermodynamic parameters [a] for the formation of carbonium ions in aqueous solution (molar scale) at 298 K

	ΔG^0_f	ΔH^0_f	S^0
H^+	0	0	0
Me^+	83·9	84·9	36·2
Et^+	61·3	54·9	43·6
Pr^{n+}	62·0	48·0	50·7
Pr^{i+}	46·5	31·9	48·6
Bu^{n+}		46·1	
Bu^{i+}		43·1	
Bu^{s+}		27·7	
Bu^{t+}	33·5	9·8 [b]	50·9
HO^-	−37·6	−55·0	−2·5

[a] ΔG^0_f and ΔH^0_f in kcal mol^{-1}, S^0 in cal K^{-1} mol^{-1}. [b] Ref. 21 gives values of $\leqslant 13$ and $\leqslant 15$.

TABLE 11

Comparison of thermodynamic reaction parameters with activation parameters [a] at 298 K

Process	ΔG^0	ΔH^0	ΔS^0	$\Delta G^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
Isobutene (g, 1 atm.) + H^+ (aq) $\longrightarrow$ Bu^{t+} (aq)	19·6	13·8	−19·3	24·9 [b]	17·0 [b]	−26·6 [b]
Isobutene (aq) + H^+ (aq) $\longrightarrow$ Bu^{t+} (aq)	16·5	19·7	10·7	22·1 [c]	22·6 [c]	1·7 [c]
Bu^tOH (aq) + H^+ (aq) $\longrightarrow$ Bu^{t+} (aq) + HO_2 (l)	21·8	31·5	32·4	27·4 [d]	34·4 [d]	23·4 [d]
Bu^tCl (aq) $\longrightarrow$ Bu^{t+} (aq) + Cl^- (aq)	14·4	18·5	14	19·5 [e]	23·1 [e]	12 [e]

[a] ΔG and ΔH in kcal mol^{-1}, ΔS in cal K^{-1} mol^{-1}; standard reaction parameters calculated from data in Table 10. [b] Observed activation parameters (ref. 47). [c] Observed activation parameters (ref. 44 and F. G. Ciapetta and M. Kilpatrick, *J. Amer. Chem. Soc.*, 1948, **70**, 639). [d] Calculated activation parameters (see ref. 44) from activation parameters for the overall back reaction and standard parameters for the overall reaction. These calculated activation parameters at 298 K can be compared with the observed parameters at 328 K, $\Delta G^\ddagger = 22{\cdot}7$, $\Delta H^\ddagger = 29{\cdot}4$, and $\Delta S^\ddagger = 22{\cdot}5$ (I. Dostrovsky and F. S. Klein, *J. Chem. Soc.*, 1955, 791). [e] Observed activation parameters (Table 8).

Table 9 are values of $\Delta P^0_f(R^+, g)$; the $\Delta H^0_f(R^+, g)$ values compare well * with other recent values.[24,39] Parameters for formation of the carbonium ions in aqueous solution follow from the values of $\Delta P^0_f(R^+, g)$, and of $\Delta P^0_7(R^+)$ and are in Table 10 together with values [40] for a few other ions. By combining data on pure substances [41] with literature data on solution of alcohols [42–45] and hydrocarbons,[17,44,46,47] values of ΔP^0_f in aqueous solution may be calculated for these solutes. Combination of such ΔP^0_f values with values of $\Delta P^0_f(R^+, aq)$ enable standard reaction parameters for a number of carbonium ion reactions in aqueous solution to be calculated.

Data on reactions involving Bu^{t+}(aq) are in Table 11, together with observed activation parameters. For reactions in which ΔH^0 and ΔG^0 are positive it follows that $\Delta H^\ddagger > \Delta H^0$ and $\Delta G^\ddagger > \Delta G^0$. Furthermore, if ΔH^0 and ΔG^0 are large in value, then from Hammond's postulate it would be expected that $\Delta H^\ddagger - \Delta H^0$ and $\Delta G^\ddagger - \Delta G^0$ would be rather small (*i.e.* that the transition state would resemble the products). Examination of Table 11 shows that these expectations are realised in all four reactions; hence the values of $\Delta P^0_f(Bu^{t+}, aq)$ and therefore those of $\Delta P^0_7(Bu^{t+})$ must be realistic ones.

Standard reaction parameters have also been calculated for reaction (11) in order to obtain data for other

$$\text{alkene (aq)} + H^+ \text{(aq)} \longrightarrow R^+ \text{(aq)} \qquad (11)$$

carbonium ions reactions. Values are in Table 12. These reaction parameters are again in accord with general principles of chemical reactivity and lend support to the values of $\Delta P^0_f(R^+, aq)$ and $\Delta P^0_7(R^+)$ obtained in this work. For example, it can be seen that Markownikoff addition to propene is favoured by 16 and to isobutene by 33 kcal mol^{-1} in aqueous solution at 298 K.

TABLE 12

Alkene	R^+	ΔG^0/ kcal mol^{-1}	ΔH^0/ kcal mol^{-1}	ΔS^0/ cal mol^{-1} K^{-1}
Isobutene	Bu^{i+}		53	
But-1-ene	Bu^{n+}		52	
Propene	Pr^{n+}	44	48	14
Ethylene	Et^+	42	46	14
trans-But-2-ene	Bu^{s+}		36	
cis-But-2-ene	Bu^{s+}		35	
Propene	Pr^{i+}	28	32	12
Isobutene	Bu^{t+}	17	20	11

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* The $\Delta H_f°(R^+)$ values in Table 9 do not agree well with values given by Franklin.[38] This is because Franklin's values are based on rather old values for $\Delta H_f°(R\cdot)$ and for the ionisation potentials of alkyl radicals.

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